

Claims

What is claimed is:

1. A method of producing high purity ammonium dimolybdate from low grade molybdenite concentrates comprising:
 - a) forming an aqueous slurry of said low grade molybdenite concentrates;
 - b) oxidizing said slurry in an atmosphere containing free oxygen at an pressure of at least about 50 p.s.i. and at a temperature of at least about 200°C and thereafter producing a first discharge with greater than about 99% of the molybdenum in said low grade molybdenite concentrates oxidized and greater than about 80% of molybdenum values insoluble;
 - c) filtering said first discharge to produce a first liquid filtrate containing soluble molybdenum values and a first solid filter cake containing the insoluble molybdenum values;
 - d) leaching said first solid filter cake with an alkaline solution to produce a second discharge wherein greater than about 98% of the insoluble molybdenum values are solubilized;
 - e) filtering said second discharge to produce a second liquid filtrate and a second solid filter cake;
 - f) recovering the molybdenum values from said second liquid filtrate by solvent extraction with an organic solvent to produce a first liquor;
 - g) crystallizing said first liquor containing the extracted molybdenum values to produce crystals and a second liquor; and then
 - h) recovering said high purity ammonium dimolybdate suitable as a chemical grade product from said crystals.
2. The method of claim 1 further comprising recycling a portion of said first discharge produced in step (b) back to the aqueous slurry in step (a).
3. The method of claim 1 further comprising subjecting said first liquid filtrate produced in step (c) to a cementation process to recover copper values, said cementation process comprising

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- adding iron to said first liquid filtrate and mixing to produce a first solution, filtering said first solution to produce a third liquid filtrate and a third solid filter cake, and then recovering said copper values from said third solid filter cake.
4. The method of claim 3 further comprising subjecting said third liquid filtrate to a molybdenum precipitation process to recover molybdenum values, said molybdenum precipitation process comprising increasing the pH level and the temperature in said third liquid filtrate, adding iron to said third liquid filtrate and mixing to produce a second solution, and filtering said second solution to produce a fourth solid filter cake containing said recovered molybdenum values.
 5. The method of claim 4 further comprising recycling said fourth solid filter cake back to said aqueous slurry in step (a).
 6. The method of claim 1 further comprising subjecting said first liquid filtrate produced in step (c) to a molybdenum precipitation process to recover molybdenum values, said molybdenum precipitation process comprising increasing the pH level and the temperature in said first liquid filtrate, adding iron to said first liquid filtrate and mixing to produce a solution, and filtering said solution to produce a third solid filter cake containing said recovered molybdenum values.
 7. The method of claim 6 further comprising recycling said third solid filter cake back to said aqueous slurry in step (a).
 8. The method of claim 1 wherein the leaching step (d) comprises an initial leach with sodium carbonate wherein the insoluble molybdenum values are solubilized and a final leach with sodium hydroxide wherein soluble iron is eliminated.
 9. The method of claim 8 wherein the pH level in the initial leaching step is maintained below about 7.0.
 10. The method of claim 9 wherein the pH level in the final leaching step ranges from about 9.0 to about 10.0.
 11. The method of claim 1 wherein the recovering step (f) comprises:

- a) contacting said second liquid filtrate with said organic solvent to form a two-phase mixture;
- b) simultaneously reducing the pH level in said two-phase mixture such that the molybdenum values in said second liquid filtrate are extracted into said organic solvent; and
- c) stripping said organic solvent to recover the molybdenum values.
12. The method of claim 11 wherein the organic solvent contains a secondary amine.
13. The method of claim 12 wherein the organic solvent contains di,tridecyl amine.
14. The method of claim 11 wherein the reduced pH level in said two-phase mixture ranges from about 4.0 to about 4.5.
15. The method of claim 11 wherein the reducing step is accomplished by adding hydrated sulfuric acid to said two-phase mixture.
16. The method of claim 11 wherein the stripping step uses ammonium hydroxide to recover the molybdenum values.
17. The method of claim 11 wherein the pH level during the stripping step is maintained at about 9.0.
18. The method of claim 1 further comprising aging said first liquor produced in step (f) before said first liquor advances to the crystallization step (g).
19. The method of claim 1 wherein the recovering step (h) includes calcining said crystals.
20. The method of claim 1 further comprising recovering chemical grade molybdenum oxide from said high purity ammonium dimolybdate produced in step (h).
21. The method of claim 1 further comprising subjecting a portion of said second liquor produced in step (g) to a rhenium extraction process to recover rhenium values.
22. A method of producing high purity ammonium dimolybdate from low grade molybdenite concentrates comprising:
- a) forming an aqueous slurry of said low grade molybdenite concentrates;
- b) oxidizing said slurry in an atmosphere containing free oxygen at an pressure of at least about 50 p.s.i. and at a temperature of at least about 200°C and thereafter

- producing a first discharge with greater than about 99% of the molybdenum in said low grade molybdenite concentrates oxidized and greater than about 80% of molybdenum values insoluble;
- c) separating and filtering said first discharge to produce a first liquid filtrate containing soluble molybdenum values and a first solid filter cake containing the insoluble molybdenum values;
 - d) leaching said first solid filter cake with an ammoniacal solution to produce a second discharge wherein greater than about 98% of the insoluble molybdenum values are solubilized;
 - e) filtering said second discharge to produce a second liquid filtrate and a second solid filter cake;
 - f) aging said second liquid filtrate;
 - g) crystallizing said second liquid filtrate to produce crystals and a first liquor; and
 - h) recovering said high purity ammonium dimolybdate suitable as a chemical grade product from said crystals.

23. The method of claim 22 further comprising recycling a portion of said first discharge produced in step (b) back to the aqueous slurry in step (a).
24. The method of claim 22 further comprising subjecting said first liquid filtrate produced in step (c) to a solvent extraction process to recover molybdenum values, said solvent extraction process comprising contacting said first liquid filtrate with an organic solvent to form a two-phase mixture, simultaneously reducing the pH level in said two-phase mixture such that the molybdenum values in said first liquid filtrate are extracted into said organic solvent, and stripping said organic solvent to produce a second liquor containing the recovered molybdenum values.
25. The method of claim 24 wherein the organic solvent contains a secondary amine.
26. The method of claim 25 wherein the organic solvent contains di,tridecyl amine.
27. The method of claim 24 wherein the reduced pH level in said two-phase mixture ranges from about 4.0 to about 4.5.

28. The method of claim 24 wherein the reducing step is accomplished by adding hydrated sulfuric acid to said two-phase mixture.
29. The method of claim 24 wherein the stripping step uses sulfuric acid to recover the molybdenum values.
30. The method of claim 24 wherein the pH level during the stripping step is maintained at about less than 3.0.
31. The method of claim 24 further comprising recycling a portion of said second liquor back to the aqueous slurry in step (a).
32. The method of claim 24 further comprising subjecting said second liquor to a cementation process to recover copper values, said cementation process comprising adding iron to said second liquor and mixing to produce a first solution, filtering said first solution to produce a third liquid filtrate and a third solid filter cake, and then recovering said copper values from said third solid filter cake.
33. The method of claim 22 further comprising subjecting said first liquid filtrate produced in step (c) to a cementation process to recover copper values, said cementation process comprising adding iron to said first liquid filtrate and mixing to produce a first solution, filtering said first solution to produce a third liquid filtrate and a third solid filter cake, and then recovering said copper values from said third solid filter cake.
34. The method of claim 22 wherein the ammoniacal solution is ammonium hydroxide.
35. The method of claim 22 wherein the ammoniacal solution is ammonium hydroxide and anhydrous ammonia.
36. The method of claim 22 wherein the aging step (f) further comprises adding a reagent to said second liquid filtrate wherein said reagent is selected from the group consisting of iron molybdate, ammonium sulfide, sulfide compounds, and ferric sulfate.
37. The method of claim 22 further comprising recovering chemical grade molybdenum oxide from said high purity ammonium dimolybdate produced in step (h).

38. The method of claim 22 wherein the crystallizing step (g) further comprises subjecting a portion of said first liquor to a second crystallization process to recover technical grade ammonium dimolybdate.
39. The method of claim 38 further comprising recovering technical grade molybdenum oxide from said technical grade ammonium dimolybdate.
40. The method of claim 22 further comprising recycling a portion of said first liquor produced in step (g) back to the leaching step (d) to precipitate impurities.
41. A method of producing high purity ammonium dimolybdate from low grade molybdenite concentrates comprising:
- forming an aqueous slurry of said low grade molybdenite concentrates;
 - oxidizing said slurry in an atmosphere containing free oxygen at an pressure of at least about 50 p.s.i. and at a temperature of at least about 200°C and thereafter producing a first discharge with greater than about 99% of the molybdenum in said low grade molybdenite concentrates oxidized and greater than about 80% of molybdenum values insoluble;
 - leaching said first discharge with an alkaline solution to produce a second discharge wherein greater than about 98% of the insoluble molybdenum values are solubilized;
 - separating and filtering said second discharge to produce a liquid filtrate containing soluble molybdenum values and a solid filter cake containing the insoluble molybdenum values;
 - recovering the molybdenum values from said liquid filtrate by solvent extraction with an organic solvent to produce a first liquor;
 - crystallizing said first liquor containing the extracted molybdenum values to produce crystals and a second liquor; and then
 - recovering said high purity ammonium dimolybdate suitable as a chemical grade product from said crystals.
42. The method of claim 41 further comprising recycling a portion of said first discharge produced in step (b) back to the aqueous slurry in step (a).

43. The method of claim 41 wherein the leaching step (c) comprises an initial leach with sodium carbonate wherein the insoluble molybdenum values are solubilized and a final leach with sodium hydroxide wherein soluble iron is eliminated.
44. The method of claim 43 wherein the pH level in the initial leaching step is maintained below about 7.0.
45. The method of claim 44 wherein the pH level in the final leaching step ranges from about 9.0 to about 10.0.
46. The method of claim 41 wherein the recovering step (e) comprises:
- a) contacting said liquid filtrate with said organic solvent to form a two-phase mixture;
 - b) simultaneously reducing the pH level in said two-phase mixture such that the molybdenum values in said liquid filtrate are extracted into said organic solvent; and
 - c) stripping said organic solvent to recover the molybdenum values.
47. The method of claim 46 wherein the organic solvent contains a secondary amine.
48. The method of claim 47 wherein the organic solvent contains di, tridecyl amine.
49. The method of claim 46 wherein the reduced pH level in said two-phase mixture ranges from about 4.0 to about 4.5.
50. The method of claim 46 wherein the reducing step is accomplished by adding hydrated sulfuric acid to said two-phase mixture.
51. The method of claim 46 wherein the stripping step uses ammonium hydroxide to recover the molybdenum values.
52. The method of claim 46 wherein the pH level during the stripping step is maintained at about 9.0.
53. The method of claim 41 further comprising subjecting said liquid filtrate produced in step (d) to a rhenium extraction process to recover rhenium values.
54. The method of claim 41 further comprising recovering chemical grade molybdenum oxide from said high purity ammonium dimolybdate produced in step (g).

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